LBNL-43601

Submitted for publication in
Applied Physics Letters

Electron Emission from Carbon Nanotubes and *ta*-C Coated Nanotubes*

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June 1999

* This work was supported by in part by a NASA SBIR Phase I grant and by the Director, Office of Science, Office of Basic Energy Sciences of the US Department of Energy under Contract Number DE-AC03-76SF00098

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Abstract

The field emission properties of multi-wall carbon nanotube films with and without a coating of tetrahedrally bonded amorphous carbon (*ta*-C) were investigated. Voltage thresholds of 2.3 V/μm for uncoated films and 1.3 V/μm for *ta*-C coated films were found. The results for the uncoated films are in good agreement with previous measurements of field emission from carbon nanotubes. The effect of the *ta*-C coating on the emission properties is discussed in the light of current field emission models.

Carbon nanotubes consist of single sheets of graphite with a tubular structure. Single-walled nanotubes are 1-2 nm in diameter; multi-walled nanotubes are typically 2-30 nm in diameter[1-3] Carbon nanotubes have been the object of increasing scientific interest[1,4] due to their unique electrical properties. Recent work on the electronic characterization of single- and multi-wall nanotubes has indicated that they hold great potential as electron field emitters[5-11], but the physics of the electron emission is far from understood

It has been shown previously that tetrahedrally bonded amorphous carbon (*ta*-C), also called diamond-like carbon (dlc) or amorphous hard carbon, has desirable field emission properties and that the emission threshold is strongly dependent on the *ta*-C chemical bonding characteristics[12,13]. *ta*-C has been proposed as a field emitting material for flat cathode configurations and has been shown to lower the voltage threshold for electron emission from metal tips[14]. We investigate here the emission characteristics of carbon nanotube films prepared from powders coalesced together as a layer on a metal substrate and the emission of the same material after coating with t-aC.

Multi-walled carbon nanotubes (MWNT) produced by MER Corp. were used in this study. The nanotubes were produced using an arc process with a graphite anode, which was evaporated in inert gas at near-atmospheric pressure. The deposit consisted of a rough, gray fused carbon "shell" that surrounds the "core". The core contained 20-40% MWNT, as determined by transmission electron microscopy. The tubes were straight with diameters between 7 and 12 nm and the walls were made of 5-50 layers of concentric graphene layers. The MWNT lengths varied from 0.5 to about 10μm and they had capped ends. The material prepared in the arc process was ground and sieved to a particle size smaller than 50 μm. This powder was then transferred and attached to a metal foil using a silver conductive epoxy. A final drying process was carried out in vacuum at 150ºC. This preparation resulted in a small

increase in the MWNT content, but the final material used for the emission measurements consisted of a mixture of the nanotubes with other carbon phases.

Our cathodic arc deposition process and its use for forming *ta*-C films been described in detail elsewhere[15,16]; only a brief overview will be given here. The ta-C films were deposited using a filtered cathodic arc plasma source operated in a pulsed mode with a repetition rate of 1 pulse per second. During the 5 ms plasma deposition pulse, the substrate was pulse-biased to –2 kV with a 125 kHz pulse-train (25% duty cycle, pulses with 2 μs on-time and 6 μs off-time). This process results in *ta*-C films with sp^3 content of 50% and a density of 2.3 g cm^{-3}. Note that the *ta*-C films formed in this way are hydrogen-free, in contrast to the hydrogenated films formed using hydrocarbon gas precursors.

Field emission measurements were carried out in vacuum at a background pressure of 2 x 10^{-8} to 5 x 10^{-8}. The sample was positioned on a horizontal platform that was connected to a dc power supply. The anode consisted of a truncated cone with an end diameter of 1.25 mm. It was mounted to the end of a micrometer vacuum feed-through that allowed the cathode-anode distance to be varied. In addition to vertical motion, the anode could also be translated on the horizontal plane, allowing us to obtain multiple measurements at various locations of the same sample surface.

Generally in measurements of this kind, the cathode-anode spacing is determined by direct reading of the micrometer with respect to a reference position at which electrical contact is established between anode and cathode (i.e., the nominal zero). Here, however, in order to prevent modification of the emitting surface, we did not allow the anode to touch the nanotube sample surface. We used the following procedure to establish the tip to sample distance. The threshold voltage required to obtain a current of $1x10^{-8}$ A was measured at several nominal spacings (d_{nom}). Plots of the threshold voltage vs. d_{nom} yield a straight line (Fig. 1). The

intercept of the plot (the distance at which zero voltage yields the threshold current) defines the offset required to convert d_{nom} to the true tip to sample distance d_{actual}. We then define the nominal electric field at the sample to be $E = V/d_{actual}$.

Field emission current-voltage curves were measured for uncoated nanotube samples and for nanotube samples coated with a 20 nm and 50 nm thick film of *ta*-C. For each sample, 144 I-V curves were measured to verify the reproducibility of the measurement and to properly determine the distance between cathode and anode during the measurements. An accurate determination of the inter-electrode distance allows the results to be presented as current *vs* electric field data. This form of data presentation provides a good means of comparison with other results from the literature, particularly when the measurements are carried out using a small inter-electrode distance and rough cathode surfaces, where the uncertainties in distance calibration can be high.

The *I-E* curves for the uncoated sample and the 30 nm coated sample are shown in Figure 2, where the entire set of experimental data is shown as small symbols in the background, and the mean values are shown as larger symbols. The advantage of plotting *I-E* curves instead of *I-V* curves is that *I-V* curves obtained at several different spacings can be superimposed for improved statistics. The difference between the *ta*-C coated nanotubes and the uncoated nanotubes is clear: field emission starts at significantly lower electric field strength for the *ta*-C coated material.

The *turn-on* field, E_{TO}, defined as the macroscopic field needed to produce a current density of 10 μA cm^{-2}, is often used as a comparison between published data. The electric field at the previously defined voltage threshold differs from the *turn-on* field (in fact, the current density at the *turn-on* field is significantly higher than that at the *threshold field*). E_{TO} values of 2.4 and 1.5 V/μm were found for the uncoated and *ta*-C-coated with 20 nm samples, respectively. This

compares well with the results of Bonard and coworkers[6], who found E_{TO} for uncoated samples in the range of 1.5 - 4.5 V/μm. The turn-on fields determined here have a significantly smaller uncertainty, and the value for the *ta*-C coated sample is less than that previously reported.

The Fowler-Nordheim theory, which has been successful in describing electron field emission from metallic surfaces, determines a relationship between the current I and electric field E given as $I \propto (\beta^2 E^2 / \phi) e^{B\phi^{3/2}/\beta E}$, where β is the field amplification factor, ϕ is the work function, and B is a constant (6.83 x10^9 V.eV$^{-3/2}$ m^{-1}). The average *I-E* curves obtained from the data shown in Figure 2 (large symbols) are shown as Fowler-Nordheim plots in Figure 3, i.e. I/E^2 as a function of E^{-1}. The curves indicate that the emission does not follow Fowler-Nordheim emission behavior over the entire range of electric field tested. For current densities lower than 25 μA/cm^2, both samples can be fitted with a constant F-N slope (straight line in Figure 3), but the fit is obviously not appropriate at higher current densities, and a lower current than that predicted by F-N is measured at high fields. Similar behavior has been founded for the uncocated MWNT [17], i.e. declining values of the slopes in the F-N plots in the high current regions. Several reasons have been used to explain changes in slope of F-N plots that can be used to explain the behavior observed here. The presence of space charges around the tip actually reduces the actual electric field at the emitting site [18]. Saturation of the emitter current can add to the space charge effect [6,18]. Recent measurements by other groups have shown that emission from single-wall nanotube films reaches saturation above 10 – 100 μA/cm^2 [6], and it is possible that saturation is occuring here as well since the deviation from linearity occurs for a current density of 50 μA/cm^2.

Several models have been postulated to explain the low emission threshold from nanotubes[3,19], although a generally accepted description is not yet available. Explanations based on the negative electron-affinity of diamond have now been mostly ruled out[20,21]. The case of 'bare' nanotubes is complex, and changes in emission properties after *ta*-C deposition

may result from several causes. *ta*-C is a semiconductor with bandgap varying from 1 to 4 eV, and containing sp^3 and sp^2 sites[21]. Dangling bonds and odd-membered rings of sp^2 sites increase the density of π states in the gap[21], therefore decreasing the resistivity. The deposition of *ta*-C may change the sp^2 content at the surface, and therefore the emission properties. Also, due to the complex surface topography of the nanotube film, it is highly likely that the *ta*-C film is not conformal over the entire surface, and in fact there could be areas that are not coated at all. In addition, because the deposition makes use of 2 keV C^+ ions (for part of the time), structural damage to the nanotubes and consequent changes in emission properties are likely. Density-of-states calculations of the electronic structure have shown that nanotubes can be either metallic or semiconducting depending on their structure or diameter[22], and the electronic structure varies locally in the nanotube from the cap to the lateral walls. Thus damage due to the energetics of the deposition process can account for structural changes in the nanotubes, and therefore changes in the emission properties. Moreover, differentiated coating or ion induced damage may explain the decrease of E_{TO} found in the coated samples in view of the recently proposed mechanism of chemical inhomogeneity[21] for electron emission.

An additional experiment was then carried out in an attempt to determine whether the ion damage could account for the observed phenomenon. The sample of MWNT coated with a 50 nm *ta*-C helps us to explain the effect of the *ta*-C deposition. The I-V curve from this sample is not plotted in Figure 2 because it coincides with that of the uncoated MWNT sample. The actual thickness of the *ta*-C film on the rough surface is virtually unknown because of the surface roughness and morphology of the sample surfaces, and these values 20 and 50 nm should be regarded as maximum thickness. The thickness increase was achieved by carrying out the *ta*-C deposition for a duration 2.5 times longer. Increasing the deposition time leads to increased probability of complete *ta*-C coating over the entire surface, and therefore increased probability of having a chemically homogeneous surface. On the other hand, ion-damage should increase as well with increasing the nominal thickness for it is cumulative. Therefore if

ion-damage is causing the enhanced emisson, we would expect the 50 nm-coated MWNT to perform even better than the 20 nm-coated one. In view of this result it is likely that the decrease in threshold voltage is due to the fact that here are more inhomogeneities at the surface of the nanotubes (coated and uncoated regions).

The results described here demonstrate that films of carbon nanotubes have good electron field emission characteristics, with a turn-on electric field strength of 2.4 V/μm, and that *ta*-C-coated nanotube films have a yet lower turn-on field of 1.5 V/μm. Such a decrease in turn-on field is lost if MWNT samples are treated with thicker (>50 nm) films.

This work was supported by in part by a NASA SBIR Phase I grant and by the US Department of Energy under Contract Number DE-AC03-76SF00098.

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Figure Captions

Fig. 1 Threshold voltage as a function of cathode-anode spacing for carbon nanotube films and *ta*-C-coated nanotube films. (Aluminum substrate).

Fig. 2 Electron field emission for MWNT films and 20 nm *ta*-C-coated MWNT films as a function of applied electric field strength.

Fig. 3 Fowler-Nordheim plot for MWNT films and 20 nm *ta*-C-coated MWNT films .

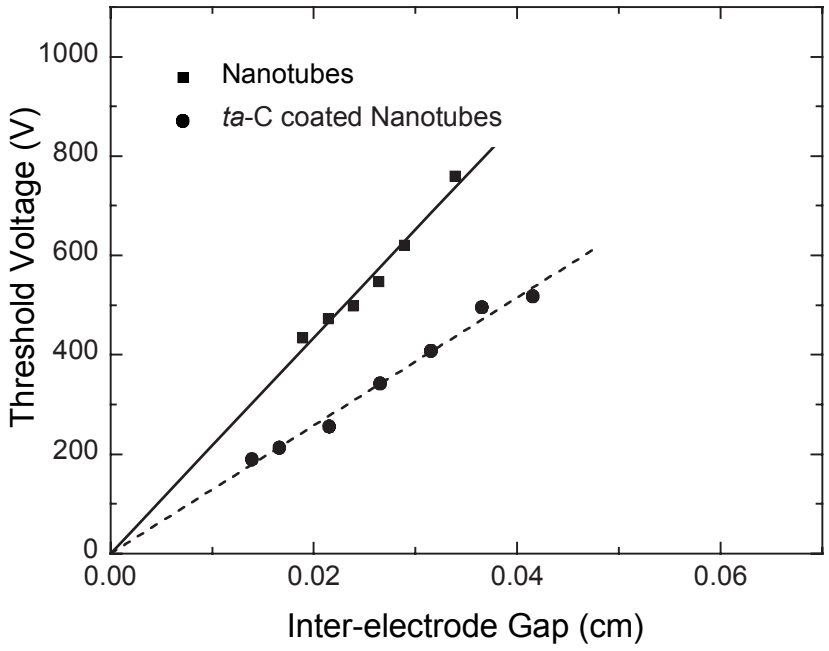
Nanotubes
ta-C coated Nanotubes
Threshold Voltage (V)
Inter-electrode Gap (cm)
0
200
400
600
800
1000
0.00
0.02
0.04
0.06

Figure 1

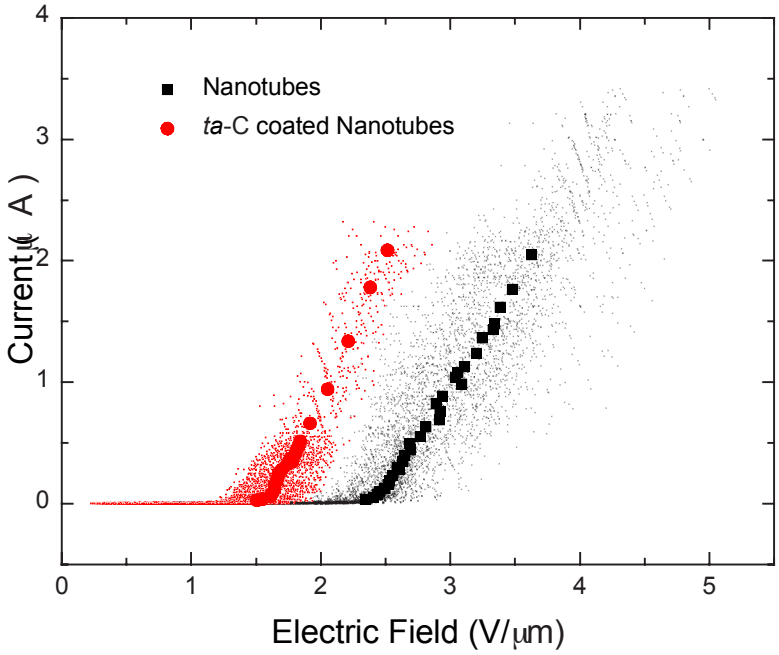
Nanotubes
ta-C coated Nanotubes
Current (μA)
Electric Field (V/μm)
0
1
2
3
4
5

Figure 2

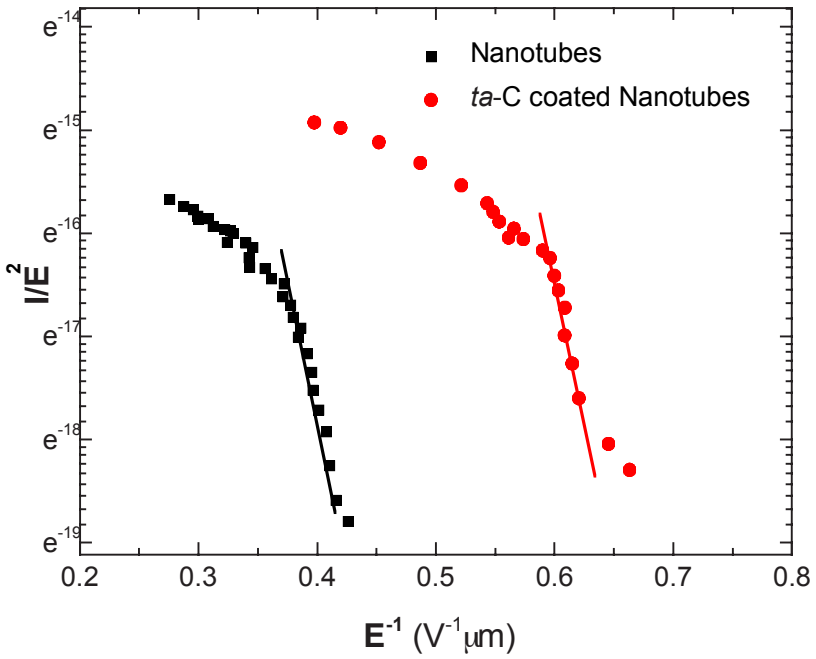
Nanotubes
ta-C coated Nanotubes
I/E2
E-1 (V-1μm)
e-14
e-15
e-16
e-17
e-18
e-19
0.2
0.3
0.4
0.5
0.6
0.7
0.8

Figure 3